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## Heterogeneous organocatalysts composed of microporous polymer networks assembled by Tröger's base formation\*\*

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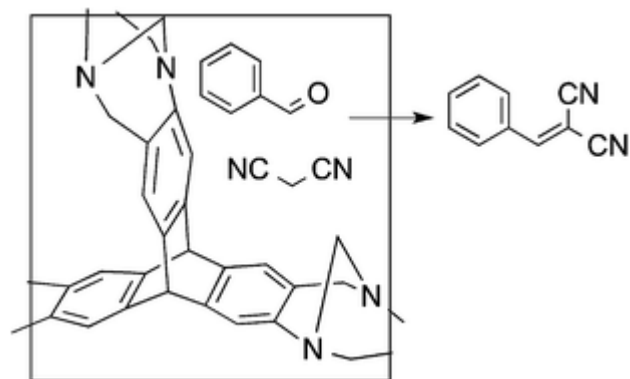
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## ARTICLE

# Heterogeneous organocatalysts composed of microporous polymer networks assembled by Tröger's base formation

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Microporous polymer networks are assembled from triamino-triptycene monomers using a polymerisation reaction based on the formation of Tröger's base (TB). The highly rigid triptycene units ensure that the polymer networks demonstrate significant intrinsic microporosity as demonstrated by apparent surface areas of up to 1000 m<sup>2</sup> g<sup>-1</sup>. These networks act as heterogeneous basic catalysts which enhance greatly the rate of a model Knoevenagel reaction between malononitrile and benzaldehyde. Indeed, the microporous networks, which possess a high concentration of basic sites, enhance the rate of the Knoevenagel reaction even more efficiently than using Tröger's base as a homogeneous catalyst.

## Introduction

The incorporation of organic components within nanoporous materials has resulted in highly porous structures with potential for gas adsorption and storage, as demonstrated by the Metal Organic Frameworks (MOFs)<sup>1</sup> and a variety of microporous polymers.<sup>2</sup> Of growing interest has been the incorporation of catalytically active units into MOFs<sup>3</sup> and microporous polymers<sup>4</sup> due to the need to develop efficient heterogeneous catalysts with large accessible internal surface areas. In addition to the incorporation of metal-containing ligands such as porphyrins<sup>5</sup> or salens<sup>6</sup>, it is also desirable to construct nanoporous materials that are capable of performing organocatalysis. For example, nanoporous materials with strongly basic components, particularly amine-containing MOFs,<sup>7</sup> and mesoporous silicas<sup>8</sup> have been the target of numerous studies seeking to provide active sites for the catalysis of a range of reactions.

Achieving a high concentration of basic amine sites in a framework of a microporous polymer represents a challenge due to the structural requirement of providing a highly rigid framework to support porosity. Amines have been introduced onto preformed microporous hypercrosslinked polymer networks by reaction of a diamine such as ethylene diamine or piperazine with the residual chloromethyl substituents remaining from the hypercrosslinking procedure.<sup>9</sup> However, the amount of amine sites that results from this process is relatively low (~1.0 mmol g<sup>-1</sup>). Recently, a microporous polymer with a greater amine content of 5.4 mmol g<sup>-1</sup> was obtained from a Porous Polymer Network (PPN-6/PAF-1), by using similar

chemistry but at the cost of a reduction in surface area from greater than 4000 m<sup>2</sup> g<sup>-1</sup> to 1014 m<sup>2</sup> g<sup>-1</sup>.<sup>10</sup> In addition, nanoporous polymer networks, of moderate surface areas (500–750 m<sup>2</sup> g<sup>-1</sup>), produced by Sonogashira–Hagihara cross-coupling reactions have incorporated 4-dimethylaminopyridine<sup>11</sup> or Tröger's base<sup>12</sup> units to provide materials with amine contents of up to 5.0 mmol g<sup>-1</sup>.

Tröger's base (TB), or more formally 2,8-dimethyl-6H,12H-5,11-methanodibenzo[b,f][1,5]diazocine), is a bridged bicyclic amine that was first isolated in 1887 from an acid-mediated condensation reaction between *p*-toluidine and dimethoxymethane,<sup>13</sup> although its structure was first correctly elucidated in 1935.<sup>14</sup> The V-shaped rigid TB structure is notable for possessing chiral C<sub>2</sub> symmetry<sup>15</sup> and TB has been employed as a building block for various supramolecular assemblies and as a suitable scaffold for molecular replication.<sup>16</sup> Contrary to an often quoted report suggesting that TB is only weakly basic,<sup>17</sup> a more recent study based on hydrogen bonding acceptor strength established that it is strongly basic relative to other aromatic amines ( $pK_{HB}(N) = 1.15$ ).<sup>18</sup> This strong basicity is due to the constraints of the rigid bicyclic system reducing the degree of conjugation between the nitrogen lone pairs and aromatic rings. Consequently, a number of nanoporous materials containing TB as component have been investigated for heterogeneous organocatalysis.<sup>8, 19</sup>

Here we describe the simple preparation of highly microporous network polymers, prepared using TB formation as the polymerisation reaction, that contain a high concentration of amine sites (up to 8.5 mmol g<sup>-1</sup>) to provide a solid capable of acting as an efficient heterogeneous basic catalyst.



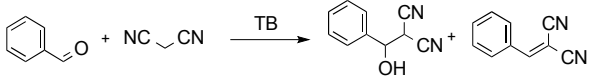
## Results and Discussions

TB and its simple derivatives can be prepared from suitable anilines in excellent yields (>95%) by their reaction with dimethoxymethane in trifluoroacetic acid (TFA), which acts as both acid catalyst and solvent.<sup>20</sup> Recently, this method of TB formation was used to prepare highly rigid, solution-processable microporous polymers, from aromatic diamines, that display promising properties for use as gas separation membranes.<sup>21</sup> Hence, it was anticipated that performing the same TB-based polymerisation reaction with aromatic triamine monomers derived from triptycene, which is a proven rigid component for generating microporosity,<sup>22</sup> would provide insoluble microporous network polymers.<sup>23</sup>

Polymer networks, PIM-TB-Trip-1 and PIM-TB-Trip-2, were prepared in good yield from 2,6(7),14-triaminotriptycene<sup>24</sup> and 2,6(7),14-triamino-9,10-dimethyltriptycene by reaction with dimethoxymethane in TFA (Scheme 1). A co-polymer network P-TB-Trip-3 was prepared similarly from 2,6(7),14-triamino-9,10-dimethyltriptycene and commercially available bis(4-amino-3-methylphenyl)methane using a 3:2 molar ratio of monomers, respectively. The resulting solids proved insoluble in all solvents and were purified by stirring in refluxing acetone, THF, chloroform and methanol. For each polymer, structural characterisation was carried out using solid state <sup>13</sup>C NMR for which spectra show the distinctive peaks associated with the TB methylene units at ~67 ppm and 59 ppm (SI Fig. 1). Elemental analysis indicates that each of the polymers have approximately the expected amount of nitrogen present (SI Table 1). Gravimetric thermal analysis (TGA) shows that the polymers contain residual solvent or water, even after heating in a vacuum oven at 50 °C, which is removed only at relatively high temperature (> 100 °C). Thermal decomposition occurs above 350 °C for each polymer.

Nitrogen adsorption isotherms collected at 77 K allow an apparent BET surface area of 1035 and 752 m<sup>2</sup> g<sup>-1</sup> to be calculated for PIM-TB-Trip-1 and PIM-TB-Trip-2, respectively, (SI Fig. 2) confirming that the fully fused-ring structures of these polymers generate microporosity. The lower value of surface area for PIM-Trip-2 is surprising as previously prepared dibenzodioxin-linked triptycene-based PIM networks with methyl substituents at the bridgehead positions had a greater BET surface area (1760 m<sup>2</sup> g<sup>-1</sup>) as compared to the equivalent network without bridgehead substituents (1318 m<sup>2</sup> g<sup>-1</sup>).<sup>22b</sup> It was proposed that these dibenzodioxin-linked networks possess a 2-dimensional structure for which the methyl groups help to increase the stacking distance between the planes. In contrast, it appears that the methyl groups of PIM-Trip-2 serve only to occupy microporosity generated by the rigid 3-D polymer framework. Network polymer P-TB-Trip-3 is non-porous (BET surface area = 1.5 m<sup>2</sup> g<sup>-1</sup>), which is unsurprising as the co-monomer, bis(4-amino-3-methylphenyl)methane, used in its preparation is not composed of fused rings and results in a more flexible network that is able to fill space more efficiently. The important physical properties of these polymers and those of related materials used previously as basic heterogeneous catalysts are given in SI Table 1. It is notable that that PIM-TB-Trip-1 has a greater concentration of amine sites than even TB itself (8.5%).

**Table 1** Data for TB-polymer mediated Knoevenagel reaction with data for TB homogeneous reaction given for comparison

						
Polymer catalyst (Molar %)	Conversion at x min (%) <sup>[a]</sup>				TON <sup>[b]</sup>	TOF <sup>[c]</sup>
	15	30	60	120		
PIM-TB-Trip-1 (1.7%)	64	82	94	100	37	2.5
PIM-TB-Trip-1 (1.0%)	38	55	74	93	35	2.3
PIM-TB-Trip-1 (0.5%)	18	33	51	72	36	2.4
PIM-TB-Trip-2 (1.7%)	61	78	90	96	36	2.4
PIM-TB-Trip-2 (1.0%)	35	52	74	89	35	2.3
PIM-TB-Trip-2 (0.5%)	16	28	47	65	34	2.3
P-TB-Trip-3 (1.7%)	24	44	64	76	14	0.9
P-TB-Trip-3 (1.0%)	14	25	41	61	14	0.9
P-TB-Trip-3 (0.5%)	7	13	24	47	14	0.9
TB (1.7%) <sup>[d]</sup>	15	29	52	73	15	1.0

[a] conversion of malononitrile from GC-MS and NMR. [b] Turnover number after 15 min. calculated from No. of moles of malononitrile consumed versus No. of mole equivalents of TB catalyst. [c] Turnover frequency calculated from turnover number per minute. [d] homogeneous reaction.

The Knoevenagel condensation reaction between benzaldehyde and malononitrile ( $pK_a = 11$ ) was chosen to assess the efficiency of the TB-containing polymer networks as a basic heterogeneous catalysis. This reaction has been used previously to test the catalytic performance of a number of materials and the corresponding data for the use of TB as a homogeneous catalyst have been reported.<sup>8</sup> Hence, following closely the published procedure,<sup>8</sup> benzaldehyde was reacted with malononitrile at ambient temperature under solventless conditions using an amount of network polymer corresponding to 1.7, 1.0 or 0.5% molar equivalents of TB. To allow for direct comparison, the evaluation of TB as a homogeneous catalyst under these conditions was also carried out and was found to demonstrate activity similar to that previously reported.<sup>8</sup>

The results of the kinetics study of the TB-polymer and homogeneous TB catalysed Knoevenagel condensation are given in Table 1 and shown in Fig. 1. Whereas the non-porous polymer P-TB-Trip-3 demonstrates similar activity to homogeneous TB, remarkably, the microporous polymers PIM-TB-Trip-1 and PIM-TB-Trip-2 demonstrate significantly higher activity. For example, the complete conversion of malononitrile is achieved by a 1.7% molar equivalent of PIM-TB-Trip-1 in 1.5 hours (94% conversion in 1 hour) whereas the same quantity of TB gives a 73% conversion in 2 hours (52% in 1 hour). Both turn-over number (TON) and turn-over frequency (TOF) indicate that that the TB units within TB-Trip-1 and PIM-TB-Trip-2 are more than twice as active when embedded within a microporous polymer than freely soluble as a homogeneous catalyst (Table 1). This enhancement of activity may be due to a rapid adsorption of malononitrile into the pore structure of these polymers, where deprotonation occurs quickly, perhaps encouraged by the close proximity of other amine units. Clearly, the microporosity of PIM-TB-Trip-1 and PIM-TB-Trip-2 appears to encourage a more rapid reaction as compared to that of the non-porous polymer P-TB-Trip-3. In addition, PIM-TB-Trip-1 demonstrates a key feature of a

heterogeneous catalyst by maintaining activity during multiple cycles of reuse, with the same sample achieving a conversion of malononitrile above 95% after eight consecutive reactions (SI Fig. 3).

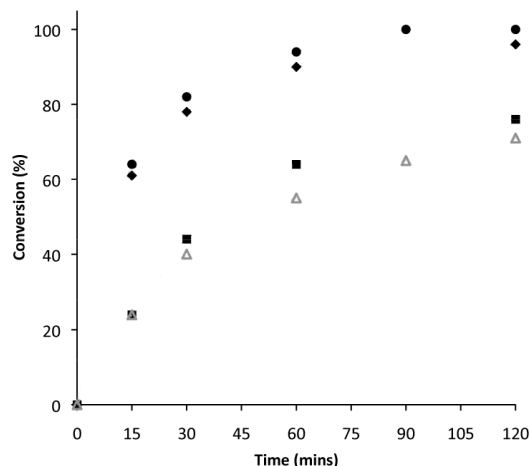


Fig. 1 Conversion of malononitrile versus time for the Knoevenagel reaction with 1.7% molar equivalents of TB for PIM-TB-Trip-1 (●); PIM-TB-Trip-2 (◆); P-TB-Trip-3 (■) and homogeneous TB (Δ).

## Conclusions

To conclude, these new microporous polymers, prepared by a simple synthetic procedure, show promise as highly active basic heterogeneous catalysts. The enhancement in activity over homogeneous TB is particularly encouraging. Although many materials have been assessed as heterogeneous catalysts for the Knoevenagel condensation reaction, direct comparisons of their reactivity is difficult due to the differences in experimental procedures. However, PIM-TB-Trip-1 and PIM-TB-Trip-2 appear to be more active than TB-containing mesoporous silicas (e.g. Si-TB-50-F),<sup>8</sup> or zeolitic-imidazole-frameworks (ZIFs)<sup>25</sup> that have been assessed under similar reaction conditions. There is an important additional advantage to the PIM-TB-Trip polymers is that, due to their high gravimetric amine content, relatively little mass of polymer is required as compared to other materials examined to date (SI Table 1).

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## Notes and references

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